May 6, 1886.

Lieut.-General STRACHEY, R.E., Vice-President, in the Chair.

In pursuance of the Statutes the names of the Candidates recommended for election into the Society were read from the Chair as follows :—

Bidwell, Shelford, M.A.
Colenso, William, F.L.S.
Dixon, Harold B., F.C.S.
Festing, Edward Robert, Major-General R.E.,
Forsyth, Andrew Russell, M.A.
Green, Professor A. H., M.A.
Horsley, Professor Victor, F.R.C.S.
Lewis, T. R., M.B.
Meldola, Raphael, F.R.A.S.

Pye-Smith, Philip H., M.D.
Russell, Henry Chamberlaine, B.A.
Unwin, Professor W. Cawthorne, B.Sc.
Warington, Robert, F.C.S.
Wharton, William James Lloyd, Captain R.N.
Wilde, Henry.

The following Papers were read :—

I. " On an Effect Produced by the Passage of an Electric Discharge through Pure Nitrogen."   By J. J. THOMSON, M.A., F.R.S., Fellow of Trinity College, Cavendish Professor of Experimental Physics, Cambridge, and R. THRELFALL, B.A., Caius College, Cambridge, Professor of Experimental Physics in the University of Sydney. Received April 13, 1886.

In the course of some experiments which we have been engaged with for some time past, on the temporary increase in the volume of a rarefied gas which takes place when an electric discharge passes through it (De la Rue and Müller, " Phil. Trans.," 1880), we found that the passage of the spark always produced permanent as well as temporary effects when the gas was nitrogen and when the pressure was less than that due to 20 mm. of mercury. The experiments described below were undertaken to clear up this point, and from them we have drawn the following conclusions :—

1. That when a succession of electric sparks of the proper kind is sent through a sealed discharge-tube containing nitrogen at a low pressure (less than 20 mm. of mercury), a permanent diminution in

the volume of the nitrogen takes place, which reaches a maximum, after which the passage of sparks of the same kind produces no permanent effect upon the volume.

2. That for nitrogen at a pressure of 8 mm. of mercury, which is the pressure at which we have usually worked, the permanent diminution in volume is from 8 to 12 per cent. of the original volume, while at a pressure of 16 mm. of mercury the diminution is not more than from 2 to 3 per cent. ; thus, though there are twice as many molecules in the tube the effect is not so big.

3. The diminution in volume takes a considerable time to reach its maximum value; in our experiments, where the discharge-tubes are 1 cm. in diameter and 25 cm. long, and the sparks were produced by an induction coil giving a spark about 4 inches long in air, it took about eight hours' sparking to produce the maximum diminution.

4. That this diminution takes place equally well whether platinum or aluminium electrodes are used.

5. That the ratio of the maximum diminution to the original volume is independent of the volume of the discharge-tube and of the extent of its surface.

6. That if the tube be maintained at a temperature of over 100° C. for several hours, the gas regains its original volume.

We attribute this diminution in the volume of the gas to the formation of an allotropic modification of nitrogen.*

We now proceed to give a detailed description of the experiments and of the various parts of the apparatus.

Discharge-tube and Gauge.

We had a good deal of trouble in getting this part of the apparatus satisfactory; we found that discharge-tubes of the ordinary kind were very liable to leak round the electrodes after a series of sparks had been passed through them. The form of tube we finally adopted is represented in fig. 1. AB is a glass tube about 25 cm. in length and 1 cm. in diameter, into which the ∪-piece E, F, G, fused up at G, is fused, sulphuric acid or mercury is placed at the bend of this ∪-tube, and serves as a gauge to measure alterations in the pressure of the gas in AB. The end B dips into a vessel containing mercury, the level of which is higher than that of the part of the tube through which the electrode passes; a piece of glass tubing is placed over the top of the discharge-tube, and the interval between the tubes caulked with glass wool; the cup thus formed is filled with mercury, which reaches above the entrance of the electrode into the tube. The electrodes are

* Since this paper was sent to the Royal Society we have seen a book by Mr. Stillingfleet Johnson, entitled "Elementary Nitrogen," in which the same conclusion is come to from purely chemical reasons.

Fig. 1.
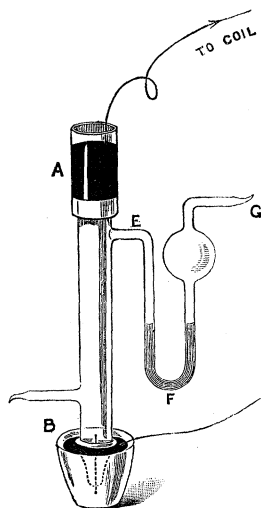
then covered with mercury, which prevents any leakage between the electrode and the tube, which we found frequently happened if this precaution was not taken. The tubes were cleaned before being used by filling them (1) with aqua regia, which was boiled in the tube, (2) with caustic potash, (3) distilled water, (4) very pure alcohol. After this they were carefully heated and dried. This was the treatment adopted for the greater part of the tubes, some of them, however, were treated with boiling sulphuric acid in addition.

The sulphuric acid in the gauge was boiled with sulphate of ammonia before being used; when the sulphate was first added to the acid, the acid became dark, but it was boiled for about half a day until it was quite colourless, and its volume about one-fourth of its original value.

The levels of the liquid in the legs of the gauge were read by a cathetometer; when the liquid was sulphuric acid the readings could be made accurately enough by placing a sheet of white paper behind the gauge and illuminating it by a gas flame. When, however, the liquid in the gauge was mercury a different course was adopted. In the first place, the gauge-tube had to be much larger to prevent mistakes arising from the sticking of the mercury to the sides of the tube. The gauge used for mercury was of the shape shown in fig. 2; the diameter of the tube where the free surface of the mercury came into contact with it was about 2 cm. A different method of reading the levels of the mercury in the legs of the gauge had also to be adopted, because it was found that when the gas flame was in front

Fig. 2.
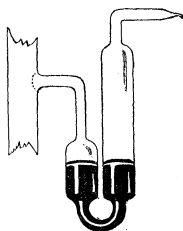
of the mercury different readings could be obtained by moving it about, the surface of the mercury was therefore illuminated from behind by a parallel and horizontal beam of light which passed through an alum cell to avoid any heating effect.

The electrodes were either platinum or aluminium, generally platinum; in some of the tubes these were fused into small pieces of glass tubing, so that only the tips of the electrodes were exposed to the nitrogen. Before being sealed the tube was connected with the pump and the gas supply in the way shown in fig. 3. After being

Fig. 3.
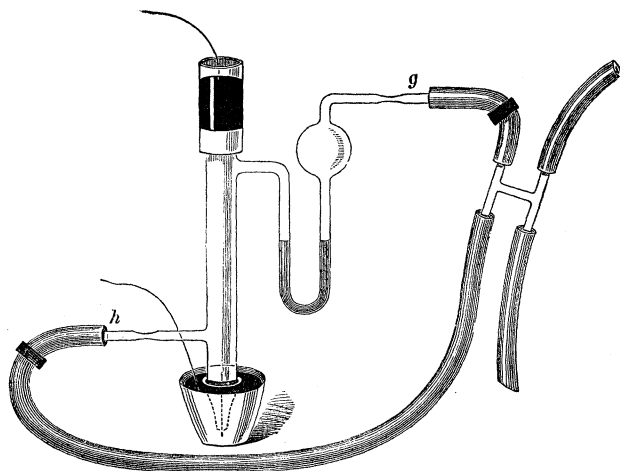
cleaned and dried, and the gauge filled either with sulphuric acid or mercury, the tube was pumped out and filled with nitrogen, and this process was repeated several times; when the pressure was very low the tube was heated to as high a temperature as it would stand without softening, in order to drive off any gas that might be on the

surface. Then a series of sparks from six very large Leyden jars charged with a Holtz machine were sent through the tube; at first when the light produced by the sparks was examined by the spectroscope the hydrogen lines were seen to be very bright, the hydrogen presumably coming out of the electrodes ; as the sparking and pumping continued the hydrogen lines diminished in brightness, and we went on sparking alternately with the Holtz and the induction coil until they had disappeared. We may mention in passing that the relative brightness of the hydrogen and nitrogen lines in a mixture of these gases is to a very large extent a question of pressure ; we found that after we had gone on sparking until there were no hydrogen lines visible at a pressure of 8 mm. of mercury, if we pumped out the gas until the pressure was reduced to 2 mm., the hydrogen lines immediately reappeared, and it required a great deal more sparking to get rid of them at this pressure. The lower the pressure the more prominent were the hydrogen lines. We went on sparking until there were no hydrogen lines visible at a pressure of 8 mm., when the sparks were produced either by the Holtz or the induction coil, and until there were no hydrogen lines visible at a pressure of 2 mm., when the sparks were produced by the induction coil. We never, however, were able to satisfy ourselves that the hydrogen lines were absent when the large sparks from the Holtz were sent through the tube at this pressure, though if they were there they were only very faint. When we had reached this stage the hydrogen lines showed no tendency to reappear when fresh nitrogen was introduced into the tube, showing that the hydrogen came from the electrodes and not from damp in the nitrogen. We found more difficulty in getting the hydrogen out of aluminium terminals than out of platinum ones. When the tube had reached this stage fresh nitrogen was let in and pumped out until the pressure in the tube was the required value, generally 8 mm. of mercury ; the tubes *g* and *h*, fig. 3, were then fused off, the gauges being watched all the time to see that there was no influx of air during this operation. When the tube had cooled the difference of level of the fluid in the ∪-tube was read by the cathetometer. It was then generally left to stand over night, and another reading taken the next day ; except in the few cases when the tube had cracked, the readings were always found to be the same as those taken on the previous evening. The tube was then ready to be experimented on.

Preparation of the Nitrogen.

The nitrogen was prepared by passing air over red-hot copper. A porcelain tube about 70 cm. long was placed on a gas furnace, it was filled with copper turnings and copper gauze ; during one-half of

the experiments the gauze was placed at the ends and the turnings in the middle, in the other half, half the tube was filled with copper turnings and the other half with gauze. The air was sucked through a tube containing pieces of pumice moistened with potash, and through a bottle half filled with the same substance, the other end of the tube was stopped by an indiarubber cork coated with paraffin, through which a glass tube passed which conducted the nitrogen to a series of bottles and tubes. These bottles and the porcelain tube were made quite air-tight; this was tested by putting the tube through which the air passed on its way to the copper in connexion with an air-pump, and exhausting down to a pressure of about 20 mm. of mercury, even with this exhaustion there was no appreciable leak through the whole arrangement of porcelain tube, drying-tubes and bottles, discharge-tubes and connexions. The porcelain tube was connected by a piece of thick-walled indiarubber tubing with a series of bottles and tubes containing purifying reagents. After leaving the copper the nitrogen passed through a potash solution in a bottle, then through two large tubes filled with carefully prepared pumice moistened with potash, it then bubbled through sulphuric acid which had been boiled down with sulphate of ammonia to about one-fourth of its original volume, it then passed through two large U-tubes filled with phosphorous pentoxide divided up into a number of layers by asbestos plugs, it then went into a large bottle about one-fourth filled with phosphorous pentoxide. All the phosphorous pentoxide used was tested and found to be free from free phosphorus. The gas after leaving the phosphorous pentoxide bottle passed through thick-walled indiarubber tubing into the discharge-tube. The volume of the tubes and bottles was very large compared with that of the discharge-tube, and as our consumption of nitrogen was slow the gas we used had stood over the phosphorous pentoxide for several days at least and often much longer. On the other hand, the gas had only been in contact with indiarubber for a short time, for the indiarubber bungs in the bottles were all coated on the inside with paraffin, and the only long piece of tubing was that leading from the last drying bottle to the discharge-tube; gas that had stood in this for more than a few minutes was always sucked out, and was never used for filling the discharge-tube.

The oxide of copper formed in the tube was reduced from time to time, in most cases by passing hydrogen through the tube; the hydrogen was generally prepared by pouring sulphuric acid on zinc, but as we suspected that a trace of sulphur dioxide which we detected had its origin in this source, we endeavoured to reduce the copper oxide by electrolytically prepared hydrogen; we could not, however, produce the hydrogen fast enough in this way, and so we finally reduced the copper oxide by carbon monoxide prepared from pure

formate of potassium; in this case the nitrogen showed no trace of sulphur dioxide, there was, however, no alteration in its behaviour in the discharge-tube.

We detected the trace of SO_2 by the change produced by the gas in the colour of paper soaked in a mixture of ferric chloride and ferric cyanide, the amount of it, however, must have been very small, as the gas produced no colouration in a paper soaked in a solution of iodide of potassium and starch, which is a very delicate test for sulphur dioxide. The diminution in the volume of the nitrogen which we observed could not have been due to the trace of SO_2, as it occurred when the copper oxide had been reduced by CO, and no trace of SO_2 was to be detected even by the ferric chloride and ferricyanide solution.

Determination of the Quantity of Oxygen in the Gas.

We were unable to detect any change of colour in a small quantity of a solution of pyrogallol and caustic potash when 50 c.c. of our gas was passed through into a eudiometer. It was thought desirable, however, to have a more perfect testing arrangement, and the following is a description of the form ultimately adopted.

FIG. 4.
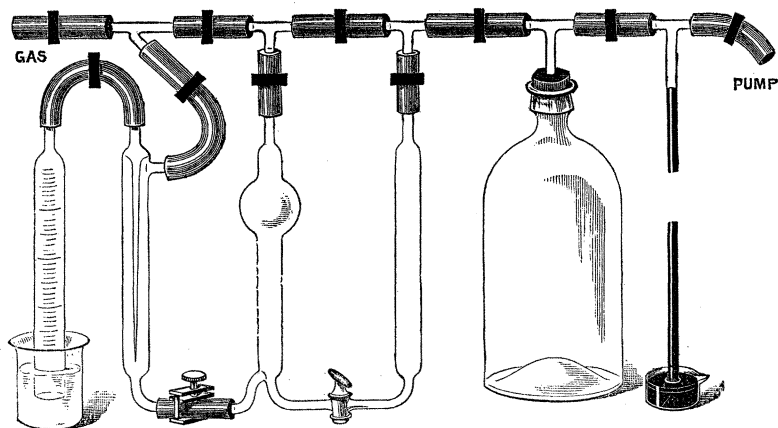
The apparatus consists essentially of four tubes and a bottle whose volume is known; by means of connexions of indiarubber tubing, taps, and clamps, each tube can be put in communication with the nitrogen supply and with the bottle separately. The tap between C and D being closed, and the tubing temporarily removed, C is filled to about half way up the bulb with carefully boiled solution of caustic

potash, and D with a solution of pyrogallol, also well boiled. The tube connexions are then replaced, and the bottle E, whose volume is large compared with that of the other parts of the apparatus, is then exhausted as far as possible by means of a water-pump. A stream of nitrogen is allowed to flow into the tubes, which are exhausted by connecting them with the bottle. After exhausting and refilling several times the tube C is left exhausted, and D in connexion with the nitrogen supply. The tap between C and D is then cautiously turned, as soon as this is down the contents of D flow over into C. As the potash solution is denser than the pyrogallol, a very perfect mixing of the fluids takes place automatically in C. As we never succeeded in getting the mixed solution colourless, it is necessary to preserve some of it as a standard for comparison. This is done by connecting B and C with the nitrogen supply together, and opening the clamp between them; the liquid then flows into B till it stands at the same level there as in C. The capacities of the tubes are arranged so that there are sensibly the same quantities of liquid in B and C, this can be done by raising or lowering B. The clamp between B and C is now closed, C put in communication with the exhausted bottle, and D in communication with the gas supply.* The pressure of the gas in the exhausted bottle is observed : suppose it is p. The tap between C and D is then opened, so as to allow a slow stream of the gas to pass from D up through C into the bottle ; as soon as a sufficient deepening of the colour has taken place in the liquid in C, the tap is turned off and the new pressure p' in the bottle noted. Knowing p and p' and the capacity of the bottle, we can calculate the quantity of gas which has flowed through the liquid in C. The stream of gas passes very slowly, and it is assumed that all the oxygen it contains has been absorbed by the liquid in C. We now require to know how much oxygen is required to produce the same change in colour, this is done by comparing the colour with that of the liquid in B. A is a pipette divided into cubic centimetres, and dipping below the surface of water contained in a beaker, the top of the pipette is connected with the delivery-tube sealed into and running down B. This tube is very fine inside B, and ends in a very fine point. In order to make the comparison of colour, the upper part of the tube is exhausted, and the clamp connecting it with the pipette slowly opened, a stream of air will pass up from the pipette into B. This process is stopped when the operator judges the colour of the liquid to be the same in B and C. The level of the water around the pipette is brought to the same level as that of the water inside, and the quantity of air taken is read off. From this we can calculate how much oxygen is required to produce the same change of colour as that

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* In the diagram the bottle is at the wrong end.

produced by the gas we are testing. We found in this way that our gas *certainly* did not contain one part of oxygen in 500, and probably not one part in 1000.

The Experiments.

A tube carefully prepared and sealed off in the way we have already described was taken, and after the cathetometer readings had shown that the pressure had remained constant for several hours, it was sparked through, generally with an induction coil. In order to get the effect we are describing, it is necessary to introduce a large resistance into the circuit, for this purpose we used a piece of wetted string, this makes the discharge through the tube much less intense and the heat produced comparatively small; we were not able to get the effect when the discharge passed straight through the tube without any resistance beyond that of the tube and the connecting wires. The fact that heat restores the gas to its original condition is sufficient to account for this, for when there is only a small resistance in the circuit, the heat developed in the tube is much greater and the tube becomes very hot. We noticed a similar thing when we used a Holtz machine instead of a coil: if we charged up five large Leyden jars with the Holtz and then discharged the jars through the tube, no permanent alteration in the pressure was observed; if, however, we never allowed the jars to get fully charged, but sent a succession of small sparks through the tube, then a permanent diminution in the volume of the gas took place.

When the discharge from the coil with a piece of wet string in the circuit went through the tube, a slow diminution in the volume of the gas took place; the rate of diminution diminished as the sparking went on and ultimately the permanent volume of the gas remained unaffected by the passage of the sparks. It took, however, a considerable time to reach this state; as a rule each tube was sparked through for between three and four hours on each of three consecutive days, the diminution in the volume at the end of the first day was about two-thirds of the maximum diminution, there was a diminution of about one-half of this on the following day, and no appreciable diminution on the third day.

The gauges of the tubes used at first were filled with sulphuric acid, and after the discharge had passed through until the pressure had become steady, it was always found that the sulphuric acid in the limb of the gauge next the tube had risen towards the tube, showing that the pressure exerted by the gas in the tube had diminished. The difference of level between the legs of the gauge increased in the case of five different tubes by from 4·5 to 7 mm.; now the pressure in the tube was originally 8 mm. of mercury, or about 58 mm. of H_2SO_4, so that the diminution in the pressure exerted by the gas is from

about 8 to 12 per cent. We thought at first that this diminution might be due to the combination of the nitrogen with the sulphuric acid vapour. In order to test this we had a tube made with a mercury gauge of the kind already described, the difference of level between the mercury in the two legs of the gauge was increased by 0·9 mm. of mercury by the sparking: 0·9 mm. of mercury are equivalent to about 6·5 of sulphuric acid, so that the magnitude of the effect is practically the same whether the guage be filled with mercury or sulphuric acid, and the effect therefore cannot be due to any combination of nitrogen with the vapour of sulphuric acid.

We then thought it might possibly be due to condensation of gas on the sides of the tube, though it seemed very improbable that this cause could produce such a large effect upon the pressure. To test this, however, we had a discharge-tube made whose diameter was about $3\frac{1}{2}$ times that of the tubes we had previously been using, so that in this case the glass was much further away from the line joining the electrodes, and in fact was so little affected by the glass that the heating was scarcely perceptible. In this case the final result was the same as for the smaller tubes, though it took longer to arrive at a state of equilibrium; the difference between the levels of the sulphuric acid in the limbs of the gauge was increased by 4·8 mm. Another reason why the diminution in pressure can scarcely be due to this cause is that it depends very much upon the pressure of the gas. We sealed off a tube at a pressure of 16 mm. of mercury, and found that when the discharge had been sent through it until the pressure had reached a steady state, the pressure had diminished only by that due to 2·5 mm. of sulphuric acid; so that the diminution is only about half the absolute value, and therefore only one-quarter of the relative value of that which takes place at a pressure of 8 mm. of mercury. It would seem to be difficult to explain this result by the hypothesis that it is due to an adhesion of gas to the surface of the glass. The experiment with the large tube shows that it cannot be due to an absorption of gas by the electrodes, for in this case the diminution in pressure would depend upon the ratio of the volume of the electrodes to the volume of the tube, so that if we increased the volume of the tube, keeping that of the electrodes the same, the effect ought to be diminished; the experiment with the wide tube showed that it is not. We also found that the effect was not diminished by using a very long tube, about three times as long as the ordinary ones.

We next tried whether the diminution in the pressure depended on the nature of the electrodes by having a tube made with aluminium electrodes, we got, however, with this tube, the same diminution as we had previously obtained with those furnished with platinum electrodes; the tube, however, was more troublesome to prepare, as the aluminium electrodes seemed to contain more hydrogen than the platinum ones.

This result shows that the decrease in pressure is not due to the formation of a compound of nitrogen and platinum, a conclusion which is confirmed by the fact that the decrease is independent of the ratio of the volume of the electrode to that of the tube.   The diminution in the pressure is too large to be explained by supposing that it is due to the formation of ammonia, which we know takes place when an electric spark passes through a mixture of nitrogen and hydrogen, for it would require at least 15 per cent. of hydrogen to be present to produce a diminution in the pressure of the gas of from 8 to 12 per cent., and we feel certain from the spectroscopic tests we have applied to the gas that the quantity of hydrogen or hydrocarbon present is extremely small, neither the hydrogen nor the hydrocarbon lines can be detected at the pressure at which we work.   Again, the gas is restored to its original pressure by keeping it for some time at a temperature just above 100° C., while ammonia is not decomposed except at a much higher temperature.

The combination of nitrogen and oxygen which takes place when a spark passes through a mixture of the two gases is attended by a diminution in volume, but we have calculated a superior limit to the quantity of oxygen present, and find that it is very much too small to explain the effects which we have observed in our tubes.

It seems to us that the effect is too big to be explained as the result of an impurity in the gas, and that the only hypothesis which agrees with the facts is that we have an allotropic modification of nitrogen produced by the passage of the sparks.   The formation of this is quite analogous to that of ozone from oxygen, and we have found that just as ozone is destroyed by continuous heating, so the diminution in pressure which we have observed in nitrogen is permanently destroyed if the tube be kept for some time at a temperature of 100° C.; we have not observed any tendency for the diminution in pressure to disappear as long as the tube is kept at the temperature of the room, about 15° C.   The diminution we have observed seems to depend even more than the formation of ozone on the kind of spark which passes through the gas, and we are disposed to attribute partly at any rate the great differences which we have observed at different pressures to this fact, at some pressures it seems impossible to get quite the right kind of spark.

We have noticed that when the electrical discharge goes through nitrogen whose pressure has been diminished by previous sparking, it has a much greater tendency to produce a beautiful golden colour than when it passes through a new tube.   Exactly (as far as we can judge) the same discharge which when it goes through a new tube will produce a bluish-pink colour, will, when it goes through an old one in which the pressure has diminished, produce a peculiar yellow colour between that of chamois leather and gold.

We have made no attempts to ascertain the chemical properties of this modified gas, and there are other points which we should have liked to develop before publishing an account of our experiments, but as one of us is leaving Cambridge for Australia it seemed advisable to publish an account of the experiments we have been able to make together.

We are indebted to Mr. Robinson for advice on some chemical points, and we cannot conclude without acknowledging how much we owe to the zeal and ability of Mr. Sinclair, the Assistant at the Cavendish Laboratory, who has done much the greater part of the large quantity of glass-blowing required for this investigation.

II. "Some Experiments on the Production of Ozone." By J. J. THOMSON, M.A., F.R.S., Fellow of Trinity College, and Cavendish Professor of Experimental Physics in the University of Cambridge, and R. THRELFALL, Caius College, Cambridge, and Professor of Experimental Physics in the University of Sydney. Received May 1, 1886.

The first experiment was made in order to see whether ozone could be formed by placing oxygen in a very strong electric field, the field, however, being just not strong enough to cause sparks to pass through the gas.

This experiment finally took the following form:—ABC is a box made of flat pieces of glass about $\frac{1}{16}$th of an inch thick, fastened together with paraffin; into the box two glass tubes, G and H, are inserted, the air entering the box through G, and leaving it through H. Against one side of the box a glass bottle, D, with flat sides, is placed and filled with water containing a little sulphuric acid, this serves as one electrode; the other electrode is a blackened tin plate, E, placed against the opposite side of the box, the distance between the electrodes being an inch and a half. The two electrodes are connected with the terminals of a Holtz machine. By altering the distance between the terminals any difference of potential can be produced between the plates. When the terminals are close together all the sparks pass between them, but when they are pulled far apart the sparks flash across the box, the discharge taking the form of a great number of separate sparks from the inside of one plate to the inside of the opposite one; the appearance of the box when the discharge passes is very pretty, it looks as if several hundred bright silver nails with broad heads were connecting the insides of the box.

The air entered the box through the tube G, having previously passed through a series of tubes and bottles filled respectively with
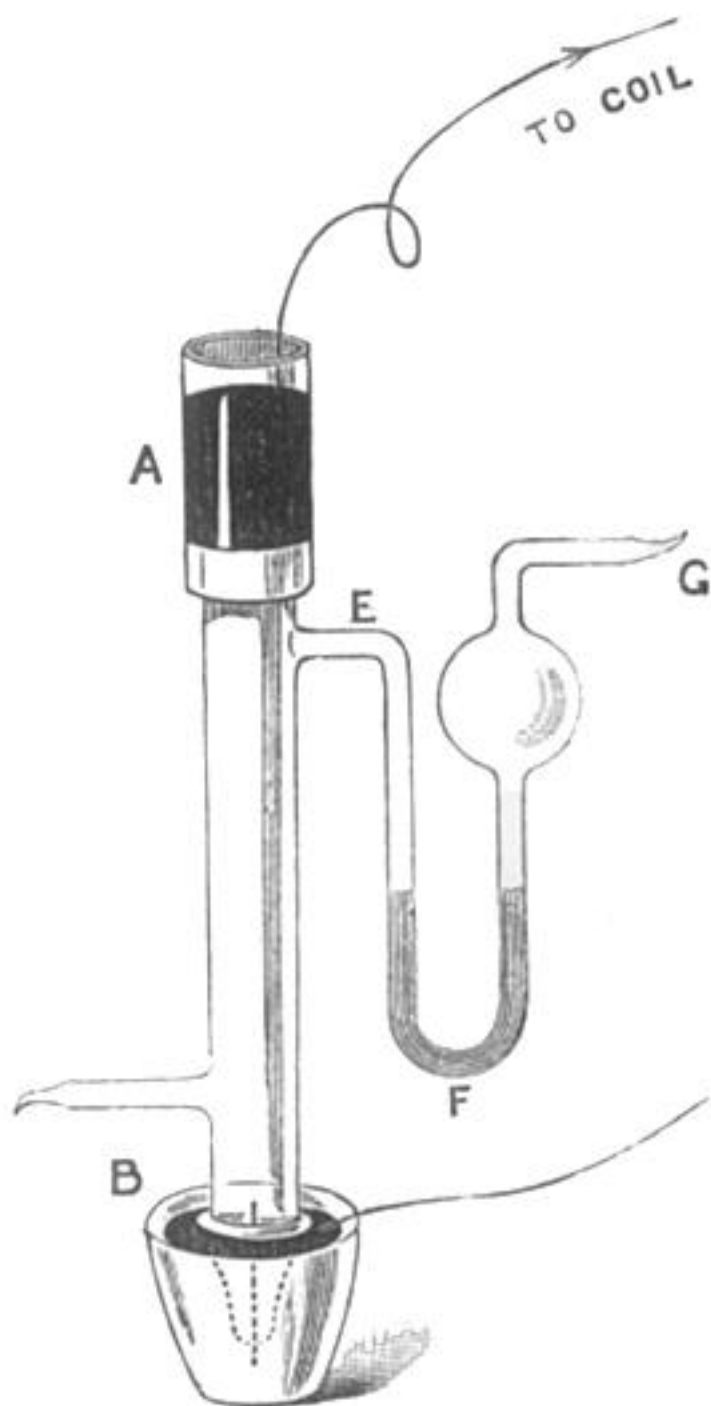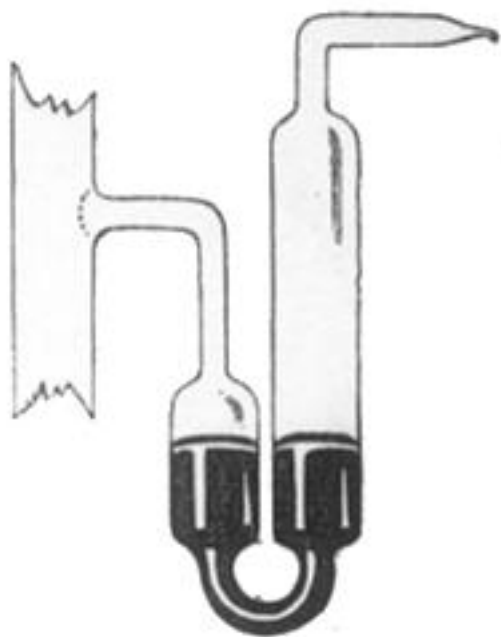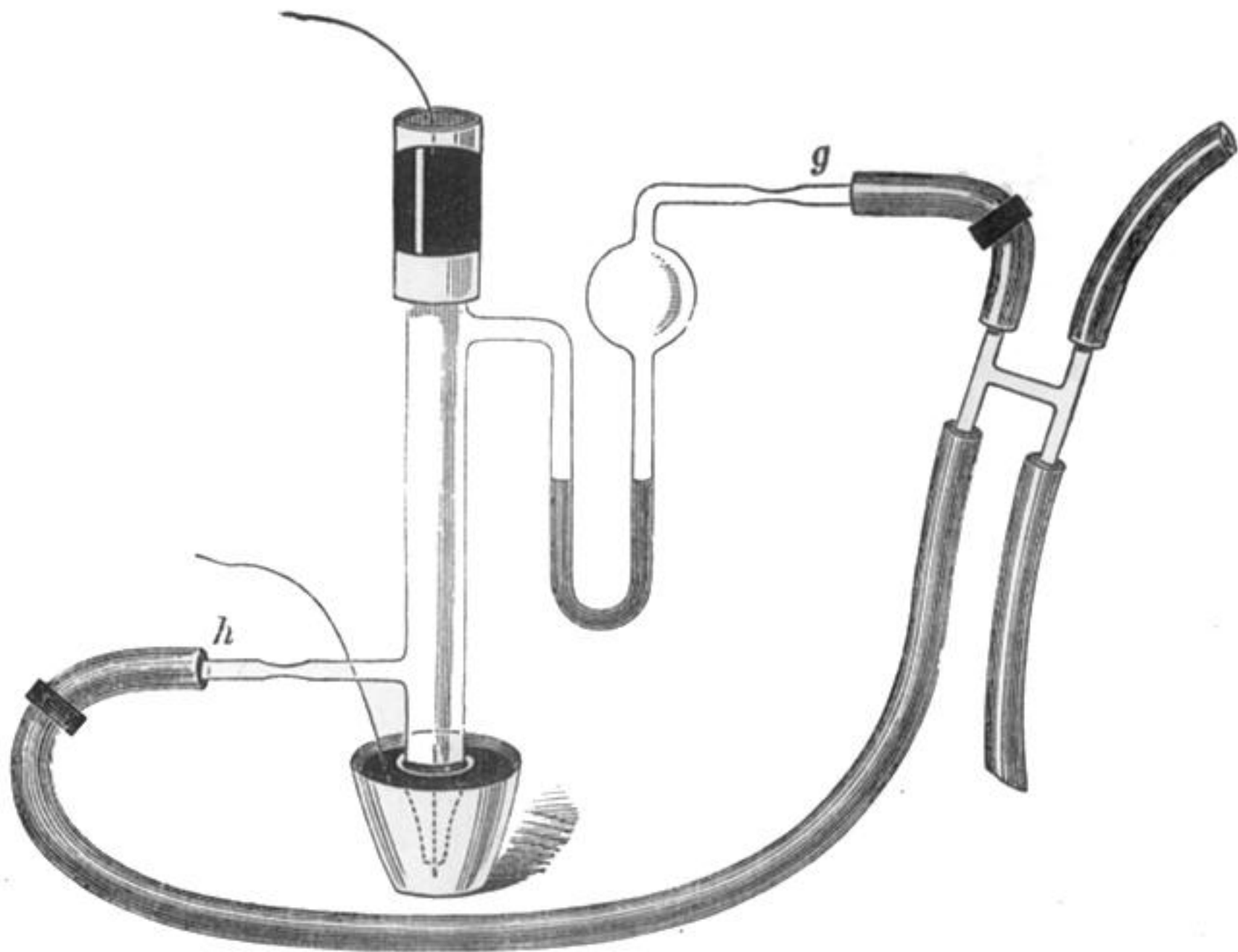
FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

GAS

PUMP